

REMARKS

Applicants have carefully considered the March 31, 2006 Office Action, and the comments that follow are presented in a bona fide effort to address all issues raised in that Action and thereby place this case in condition for allowance. Entry of the present Request for Reconsideration is respectfully solicited. It is believed that this response places this case in condition for allowance. Hence, prompt favorable reconsideration of this case is solicited.

Claims 11, 12 and 14 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Chapman, Jr. et al. (U.S. Pat. No. 5,547,761, hereinafter "Chapman") in view of Becker et al. (U.S. Pat. No. 4,454,047, hereinafter "Becker") and Hiraga et al. (U.S. Pat. No. 6,268,469, hereinafter "Hiraga") and further in view of Carey (U.S. Pat. No. 3,256,251, hereinafter "Carey"). Applicants traverse.

The Examiner asserted that Chapman teaches the process steps of claim 11, but for the settlement of the mixture following the stirring step. The Examiner stated, however, that Chapman does disclose decanting the floating polymer powder without disturbing the sediment and, therefore, the Examiner concluded that sedimentation must inherently exist because a solid phase of precipitation in the mixture, together with the liquid phase containing the floated polymer powder, is already formed. The Examiner stated that Becker teaches a removal process for oils and solids from aqueous systems and, therefore, it would have been obvious to allow for the settling of the stirred mixture (such as a copolymer dispersion) in the process of Chapman in order to allow for the formation of aqueous and non-aqueous phases as stratified layers, as suggested by Becker. The Examiner further argued that it would be reasonable to presume that the process of Chapman and Becker would apply to the preparation of polyvinylidene fluoride, as suggested by Hiraga.

In response to the arguments previously submitted on January 26, 2006, the Examiner, at page 4 of the Office action, asserted that it is known in the art that molecular weight of a resin is distributed and densities of the particles vary and, therefore, the separation method taught by the combination of Chapman and Becker would inherently possess the separation of low molecular weight resin particles in the mixture. Moreover, with respect to the step of repeating the sequence operation for the purposes of recovering the copolymer, the Examiner, at page 3 of the Office action, asserted that it would have been obvious to have this repetition to ensure complete recovery, as evidenced by Carey at col. 1, lines 48-50. With respect to dependent claim 14, the Examiner asserted that the repeating operation of not less than three (3) times, would have been obvious to one of ordinary skill in the art, absence a showing of criticality. Applicants respectfully request reconsideration and withdrawal of the rejection in view of the following remarks.

The polyvinylidene fluoride of the present invention is obtained by suspension polymerization which is explicitly required in the independent claim 11. In contrast, none of the cited documents teaches suspension polymerization, but rather only disclose emulsion polymerization. In Chapman, emulsion polymerization is employed for producing polymers from the description at col. 6, lines 3 to 7 (“dispersion (sometimes designated emulsion)”); col. 7, lines 1 to 5 (water-soluble initiators such as APS, KPS are used); col. 8, lines 27 to 37 (polymers are formed by coagulation), and col. 15, lines 5 to 6 (particle size obtained in polymerization is typically 0.05 – 0.2  $\mu\text{m}$ ). Similarly, Becker discloses that emulsions are employed as described at col. 8, lines 8 to 16. Hiraga, at col. 2, lines 17 to 32 discloses a solid-liquid separation method of an emulsified dispersion of fluorine-containing polymer particles. Carey teaches the recovery of solid resinous materials from emulsions thereof and also teaches a method of coagulating solid resinous materials from emulsions thereof. See Carey at col. 1, lines 10 to 20.

Therefore, none of the cited documents teaches the process for preparing a copolymer by suspension polymerization as required in the independent claim 11. Thus, the Examiner has failed to identify a source in the applied prior art for every claim limitation recited in independent claim 11. It is legally erroneous to ignore any claim limitation. *Uniroyal, Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 5 USPQ2d 1434 (Fed. Cir. 1988). For at least this reason, the rejection is not legally viable and should be withdrawn.

Moreover, the particle diameter of polymers obtained by emulsion polymerization is smaller than 1/100 of the particle diameter of polymer obtained by suspension polymerization. The Examiner's attention is directed the accompanying Appendix, wherein as described at pages 489 to 490 of "Modern Fluoropolymers", Edited by John Scheirs, c1997, John Wiley & Sons Ltd, the section "3 POLYMERIZATION", the particle diameter of PVDF obtained by emulsion polymerization is from 0.2 to 0.5  $\mu\text{m}$ , while the particle diameter of PVDF obtained by suspension polymerization is approximately 100  $\mu\text{m}$ .

Applicants submit that since the particle diameter of PVDF obtained by suspension polymerization is large, a dry powder is formed through the process of separation, washing and drying without granulation operation. In the suspension polymerization, the polymerization progresses from the surface toward the center in the droplet of the monomer by a certain polymerization initiator, so that the particles are formed as spheres of pearl-shape which has the minimum energy and the particle size is decided by the size of the droplet.

On the other hand, in the emulsion polymerization, a dry powder is formed through the process of separation, washing and drying after agglomeration to the secondary particles by the method as described in Hirage. That is, in the emulsion polymerization, polymerization grows on the surface of the emulsification micelle of the monomer by a certain polymerization initiator

existing on the water side. The size of micelle is 2 to 4 figures smaller than the droplet of the suspension polymerization.

It is well known to persons skilled in the art that there are distinct differences in physical properties such as shapes or density between the particles agglomerated after emulsion polymerization and the particles obtained by suspension polymerization. Therefore, it would be improper to conclude that the separation method after the emulsion polymerization is related to the separation method after suspension polymerization. It is not obvious from the separation method after emulsion polymerization to expect that the copolymer particles obtained by suspension polymerization float or precipitate in water. None of the cited documents teaches or suggest the influence that the separation of particles gives to thin film formation.

Moreover, Applicants submit that neither Chapman nor Becker, alone or in combination, teaches the separation of the copolymer particles floating in the upper part of the mixture from the copolymer particles precipitated in the lower part of the mixture. Chapman teaches the separation of a non-water-wet powder which floats on the water and Becker teaches separation of an oil phase from a water phase. Moreover, the Examiner's asserted motivation to modify the process of Chapman/Becker in view of Hiraga lacks the requisite factual basis and the requisite realistic motivation. In the present case, the Examiner is improperly assuming that the process of Chapman combined with Becker would apply to the preparation of polyvinylidene fluoride.

The requisite motivation to support the ultimate legal conclusion of obviousness under 35 U.S.C. § 103 is not an abstract concept, but must stem from the applied prior art as a whole and have realistically impelled one having ordinary skill in the art to modify a reference or combine references to arrive at a claimed invention. *In re Deuel*, 51 F.3d 1552, 34 USPQ2d 1210 (Fed. Cir. 1995); *In re Newell*, 891 F.2d 899, 13 USPQ2d 1248 (Fed. Cir. 1989). The Examiner's mere

identification of claim features in disparate references does not establish the requisite realistic motivation to support the ultimate legal conclusion of obviousness under 35 U.S.C. § 103. *Grain Processing Corp. v. American-Maize Products Co.*, 840 F.2d 902, 5 USPQ2d 1788 (Fed. Cir. 1988). Moreover, the Examiner's assumption does not establish the requisite motivation to modify a specific reference in a specific manner to arrive at a specifically claimed invention. *In re Deuel, supra*. Rather, a burden is imposed upon the Examiner to identify a source in the applied prior art for each claim limitations and identify a source for the requisite realistic motivation to modify a particular reference in a particular manner to arrive at a specifically claimed invention. *Smiths Industries Medical System v. Vital Signs Inc.*, 183 F.3d 1347, 51 USPQ2d 1415 (Fed. Cir. 1999); *In re Mayne*, 104 F.3d 1339, 41 USPQ2d 1451 (Fed. Cir. 1997).

Dependent claim 13 was rejected under 35 U.S.C. § 103(a) as being unpatentable over Chapman in view of Becker and Hiraga and further in view of Tsutsumi et al. (E.P. Pat. App. No. 0 508 802 A1, hereinafter "Tsutsumi"). Applicants note that the Examiner cited the corresponding Japanese application on the PTO-892 form for the Tsutsumi reference.

Applicants incorporate herein the arguments previously advanced in traversal of the rejection of claims 11, 12 and 14 under 35 U.S.C. § 103 predicated upon Chapman, Becker, Hiraga and Carey. Dependent claim 13 is free from the applied art in view of its dependency from independent claim 11. Accordingly, reconsideration and withdrawal of the rejection are solicited.

It is believed that pending claims 11-14 are now in condition for allowance. Applicant therefore respectfully requests an early and favorable reconsideration and allowance of this application. If there are any outstanding issues which might be resolved by an interview or an

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Examiner's amendment, the Examiner is invited to call Applicant's representative at the telephone number shown below.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

McDERMOTT WILL & EMERY LLP



Brian K. Seidleck  
Registration No. 51,321

600 13<sup>th</sup> Street, N.W.  
Washington, DC 20005-3096  
Phone: 202.756.8000 BKS:idw  
Facsimile: 202.756.8087  
**Date: June 30, 2006**

**Please recognize our Customer No. 20277  
as our correspondence address.**

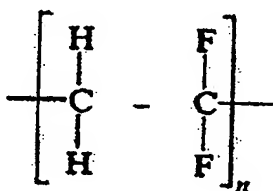
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# PVDF in the Chemical Process Industry

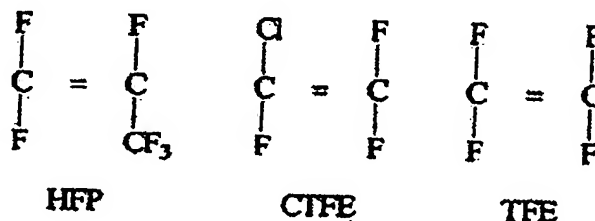
Elf Atochem North America Philadelphia, PA, USA

## 1 CHEMICAL STRUCTURE OF PVDF

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Vinylidene fluoride-based copolymers, typically called PVDF copolymers, have become the products of choice in many applications that were formerly PVDF homopolymer [1]. These copolymers have also replaced other fluoropolymers or metals in the Chemical Process Industry (CPI) where PVDF homopolymer had limitations in impact strength and elongation that prevented its use.

The most common comonomers utilized with PVDF for CPI applications are hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), and tetrafluoroethylene (TFE):



Other monomers exist that can be utilized to create VDF-based resins with interesting properties, but the above three are the most commonly used and readily available for current applications.

## 2 HISTORY OF PVDF

Polyvinylidene fluoride was first commercially introduced in 1961 by the Pennsalt Chemical Company (later known as Pennwalt Corporation now owned by Elf Atochem North America, Inc.). The original applications for the polymer still exist today. Early property evaluations of PVDF led to its use as piping and molded parts for plutonium recovery applications in nuclear facilities, abrasion-resistant insulation for computer back panel wire, and as a long life finish on metal panels used in architectural construction.

Since the original introduction by Pennsalt Chemical Co., and the first full-scale commercial plant built in Calvert City, Kentucky, USA, in 1965, several other plants were built by various companies to meet rising demand for PVDF and PVDF copolymers in many markets. Table 25.1 lists the current producers of PVDF for commercial applications worldwide.

Growth of PVDF has been fueled by several landmark applications. Heat-shrinkable tubing for electrical insulation in military applications and heat trace wiring were the original core markets in the 1960s. Strong growth in architectural finishes, plastic-lined steel for chemical plants, and fabrics for pulp and paper applications fueled large volume growth in the 1970s. In the early 1980s, the

**Table 25.1.** Producers of PVDF type products

Producer	Plant Location	Trademark
Ausimont	United States	Hylar
Daikin	Japan	Neoflon
Elf Atochem	United States	Kynar, Kynar Flex
	France	Kynar (Formerly Forafion)
Kureha Chemical Industry Co., Ltd	Japan	KF
Solvay & Cie, SA	France	Solef



largest 'overnight' market for PVDF, especially PVDF copolymers, was created when the United States National Electrical Code (NEC) called for low-smoke, low-flame polymers to be used in plenum areas of buildings as an alternative to any polymer insulation placed in conduit. This plenum cable market for PVDF caused a worldwide shortage of PVDF-type polymers which brought on new PVDF plants and expansions of existing ones.

Also, in the 1980s, high-purity semiconductor chip manufacturers started to discover that plastics outperformed metals in the transport of high-purity washing chemicals in the manufacture of computer devices. By the mid-1980s, PVDF was becoming the material of choice compared to other cheaper polymers due to the fact that it could be easily processed without the need for any processing aids, stabilizers, fillers, or additives whatsoever [2-6].

In the 1990s, PVDF-type polymers maintained growth even during recession periods and they continue to be in high demand as materials for high-purity processing components (e.g. piping, tank linings, pumps, filtration products, fittings, flexible tubing, etc), architectural coatings, and new smaller markets such as use as an additive to other polymers to improve processing or performance, films for weathering protection of vinyls, and specialty hoses for fuel containment where permeation regulations exist. The market for PVDF products in plenum cable has declined since 1990 for various reasons, but still remains as a major area of application for this polymer family. New regulations promise renewed growth in electrical applications for the next few years.

The outlook for PVDF-type resins and other fluoropolymers is excellent. Expectations are for double digit growth up to and beyond the year 2000. Since PVDF is the least expensive fluoropolymer on a cost per volume ratio, it is often the first such material considered for new arising applications.

### 3 POLYMERIZATION

Commercial polymers based on vinylidene fluoride can be categorized into two types of polymerization methods. While there are other methods of producing PVDF homopolymers and copolymers, the most common methods are emulsion and suspension polymerization.

In emulsion polymerization, a number of reactant products are used such as fluorinated surfactants, initiators, and possibly chain terminators. Some manufacturers that supply very pure PVDF products for special applications employ high-purity rinsing of the emulsion latex before final drying [7]. This washing helps to eliminate any residual impurities such as polymerization initiator and surfactant before packaging as a free-flowing powder, or processing the powder into a pellet for extrusion or injection molding applications. The particles of the polymer isolated from the reaction vessel are agglomerated spherical particles ranging in diameter from 0.2 to 0.5  $\mu\text{m}$ .

In suspension polymerizations, an aqueous recipe is used with initiators, colloidal dispersants (not always necessary), and chain transfer agents to control

molecular weight. The final suspension consists of spherical particles which are approximately 100  $\mu\text{m}$  in diameter. Suspension polymers are available either as a free-flowing powder or as a pellet for extrusion or injection molding applications.

Both emulsion and suspension PVDF in powder form can be milled into finer particle size with higher surface area for greater solubility to be used in coatings for metal components.

Comonomers such as HFP, CTFE, and TFE can be added at the start of polymerization or at other times in the reaction process to create VDF-based polymers with various crystallinities. These comonomers in existing commercial products typically impart flexibility, chemical resistance, elongation capability, solubility, impact resistance, clarity, and thermal stability in processing. On the downside, they often have lower melting points, higher permeation, lower tensile strength, and higher creep than PVDF homopolymers.

Only a small amount of comonomer is needed (less than 6%) in some cases to dramatically improve specific performance requirements if PVDF homopolymer is considered deficient. The maximum level of comonomer is limited by the phenomenon that the resin becomes an elastomer rather than a polymer if the comonomer ratio is over a certain percentage. For example, the addition of HFP at more than 20% would favor elastomeric tendencies.

PVDF for most applications does not contain additives. However, many compounded products are available for special applications. It has been found that small amounts of specially formulated PTFE can act as a process aid for PVDF-based resins. PTFE also acts as a surface lubricant that can lower the coefficient of friction of PVDF molded parts.

The addition of carbon black can be used to reduce mold shrinkage to nearly match polypropylene if the user can tolerate a black colored finished part. Glass spheres can also be compounded in PVDF for strength and shrinkage reduction, but component production must be done under a watchful eye to avoid decomposition created by the potential of silica reacting with PVDF at high processing temperatures. For products with reduced shrinkage and increased tensile strength, carbon fibers are sized with PVDF to create what is termed as carbon fiber reinforced PVDF. Commercial products exist with between 15 and 25% carbon fiber. The larger the percentage of carbon fiber, the lower the shrinkage and the higher the tensile strength and deflection temperature.

Specific smoke suppressants are available that can make certain PVDF-type resins virtually nonflammable. Typically such additives are added at levels well below 2% and do very little to change the mechanical properties of the resin. These resins that contain these additives can pass tests that few other plastics can pass. This has led to applications in institutional piping, duct work, and coatings for facilities where plastics offer an installation advantage, chemical advantage, or purity advantage over metals, but were previously not considered due to fire safety concerns.

PVDF accepts pigments and can be colored easily. Black, red, and blue resins are standard offerings and can be made from FDA listed pigments with very low percentage concentration. A whole spectrum of colors have been produced using concentrates should special colors be desired.

#### 4 PROPERTIES OF PVDF

Polyvinylidene fluoride has a great balance of properties that make it suitable for many applications. The molecular structure with alternating  $\text{CH}_2$  and  $\text{CF}_2$  groups along the polymer chain forms a unique polymer with some of the best characteristics of polyethylene ( $-\text{CH}_2-\text{CH}_2-$ )<sub>n</sub> combined with performance approaching polytetrafluoroethylene ( $-\text{CF}_2-\text{CF}_2-$ )<sub>n</sub>. The resultant polymer provides excellent properties in the following respects:

- Mechanical strength and toughness
- Resistant to fungi
- High abrasion resistance
- Low permeability to gases and liquids
- High thermal stability
- Low flame and smoke characteristics
- High dielectric strength
- Resistant to creep at elevated temperatures
- High purity
- Readily melt processable by many methods
- Resistant to most chemicals and solvents
- Rigid and flexible versions available
- Resistant to ultraviolet and nuclear radiation
- Impact resistant versions available
- Resistance to weathering
- Cold weather performance to  $-40^\circ\text{C}$

The selection of PVDF resin for given applications has become more difficult due to the broad range of grades now available. Homopolymer properties have a much smaller variation between manufacturers than the difference range now available due to the commercially available copolymers that were developed in the 1980s and early 1990s.

In applications where PVDF homopolymer may not have been considered because of impact strength, elongation at break, chemical stress cracking, lack of clarity, or lack of flexibility, PVDF copolymers meet the need that may have been deficient, and at a similar cost. A set of property tables for PVDF homopolymers,  $\text{VF}_2/\text{HFP}$  polymers, and filled PVDF resins are shown in Tables 25.2-25.4.

Compared to other commercial fluoropolymers, PVDF has the lowest melting point, but actually has the highest heat deflection temperature under load.